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Macromolecular chains subject to boundary constraints: Universal scaling amplitudes

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Universality of scaling amplitudes and, more generally, scaling functions entering the statistical description of a long self-avoiding chain confined to a d^*-dimensional region $L^{d-d^*}\times\infty^{d^*}$ is investigated. The nonuniversal microscopic details enter through metric factors which can be calculated from the bulk ($L=\infty$) data.

Scaling theory of a long self-avoiding chain or, in the lattice version, a self-avoiding walk (SAW) in restricted geometries has been formulated by Daoud and de Gennes.[1] A flexible polymer molecule confined to a d^*-dimensional "pore" $L^{d-d^*}\times\infty^{d^*}$ is considered, where L^{d-d^*} is a cross-sectional "area," while[2] $d^*=1,2,\ldots,d-1$. Several numerical verifications of the scaling hypothesis by Monte Carlo[3] (MC) and exact enumeration techniques[4,5] have been reported. Most, however, have been restricted to relatively small-L strips ($d=2,d^*=1$) or tubes ($d=3,d^*=1$).[6] More general geometries have been considered[7] within the Flory-Huggins, mean-field-type theory.

One open problem emphasized by Daoud and de Gennes[1] is that their scaling "results. . . lack precise numerical coefficients." In this Rapid Communication we establish the universality of scaling coefficients and, more generally, scaling functions which depend on d,d^*, and possibly on the boundary conditions and the precise shape of the "macroscopic" L^{d-d^*} cross section. Microscopic details of the chain structure at the "monomer" level enter through nonuniversal *metric factors* which, however, *can be determined from the bulk $L=\infty$ data.* Thus, only universal quantities must be determined by finite-size calculations which, therefore, can be performed on the simple lattice SAW models.

The lattice SAW problem has a magnetic analog:[8] the $n\to 0$ limit of the n-vector model. Our identification of the nonuniversal metric factors below invokes the recently discovered "hyperuniversality" property[9,10] in the finite-size scaling theory,[11] and is therefore restricted[9] to $d<d_c(=4)$. Fortunately, the interesting cases of $d=2$ and 3 are covered.

We consider a self-avoiding chain with the polymerization index N measured by the number of constituent units or by the number of steps of SAW, or by any other dimensionless quantity proportional to the actual length of the chain. In the fixed-N "canonical ensemble" formulation the $N\to\infty$ limit corresponds to "criticality" while N^{-1} may be viewed as a temperature-like linear scaling field[12] with the associated critical exponent ν. As usual,[12] N^{-1} will enter scaling relations with a nonuniversal metric factor which depends on the microscopic details (including the prescription for measuring N). Below the upper critical dimension, $d_c=4$ here,[8] the "pore" size L has a special property,[9] termed the finite-size hyperuniversality, that no metric factor is associated with L, which must be measured as the *actual geometrical length.*[9]

For the squared end-to-end distance, averaged over all the distinct N-step chains, $\langle R_N^2\rangle$, the large-N and L scaling form,[1]

$$\langle R_N^2\rangle^{1/2}\approx LY(aN^{-1}L^{1/\nu}) \ , \tag{1}$$

involves a *single* nonuniversal factor a. Note that $\langle R_N^2\rangle$ must be measured in the same units as L^2. If N and L are such that $\langle R_N^2\rangle \ll L^2$, the bulk behavior is found[1]

$$Y(y)\approx Y_\infty y^{-\nu}, \ \text{as } y\to\infty \ , \tag{2}$$

$$\langle R_N^2\rangle_{\text{bulk}}^{1/2}\approx a^{-\nu}Y_\infty N^\nu \ . \tag{3}$$

In the opposite limit, when $\langle R_N^2\rangle \gg L^2$, the d^*-dimensional "critical" behavior with exponent ν^* ($>\nu$, see Ref. 13) will be obtained[1,13]

$$Y(y)\approx Y_0 y^{-\nu^*}, \ \text{as } y\to 0 \ , \tag{4}$$

$$\langle R_N^2\rangle_{\text{long chains}}^{1/2}\approx a^{-\nu^*}Y_0 L^{-\nu^{-1}(\nu^*-\nu)}N^{\nu^*} \ . \tag{5}$$

Note that Y_0 and more generally the *universal* function $Y(y)$ depend on d,d^* but also on the boundary conditions and the cross-section shape. The bulk-limiting coefficient Y_∞ may depend on d only; one can choose a convenient normalization $Y_\infty=1$ by (universally) redefining $Y(y)$; however, we will keep the general notation.

Let x denote one of the d^* unbounded coordinates. Both $\langle|x_N|\rangle$ and $\langle x_N^2\rangle^{1/2}$ have been used[3,5] to measure the chain extent. Obviously, relations of the form (1)–(5), but with *different scaling functions,* apply to these quantities, and also to the rms radius of gyration. For example,

$$\langle x_N^2\rangle^{1/2}\approx LX(aN^{-1}L^{1/\nu}) \ , \tag{6}$$

where $X(y)$ and the associated coefficients X_∞ and X_0, as in (2) and (4), are universal. Note that $X_\infty=d^{-1/2}Y_\infty$ and $X_0=(d^*)^{-1/2}Y_0$, provided the problem is (microscopically) isotropic.

The nonuniversal factor a in the scaling relations (1)–(6) can be measured from the bulk ($L=\infty$) data, e.g., by using Eq. (3), for a realistic system. All the universal factors can be determined by studying lattice SAW models.

The behavior of $\langle R_N^2\rangle$ and of the rms radius of gyration have been studied extensively for SAW's on various regular $d=2$ and 3 lattices ($L=\infty$), by exact enumeration[14] and Monte Carlo[15] techniques. However, the coefficient $a^{-\nu}Y_\infty$ in relation (3) has rarely been estimated[16] because the main objectives were the exponent values. With the existing data, reliable estimates of $a^{-\nu}Y_\infty$ can be obtained by using the extrapolation techniques of Ref. 16. The main barrier to further progress, however, is the finite-size ($L<\infty$) cal-

culations for lattice SAW's. The available results[3-5] are rather inaccurate as far as estimation of numerical prefactors in relations of the form (5) are concerned. More extensive numerical studies are called for.

In the discretized or lattice version of the self-avoiding-chain problem, one can define the total number c_N of the N-step chains. This quantity scales according to

$$c_N \approx AN^{\gamma-1}\mu_\infty^N C(aN^{-1}L^{1/\nu}) \ , \tag{7}$$

where A is a new nonuniversal metric factor independent of a. The function $C(y)$ is universal, and in the bulk limit, $\langle R_N^2\rangle \ll L^2$, one anticipates

$$C(y) \approx C_\infty, \ \text{as } y \to \infty \ , \tag{8}$$

$$(c_N)_{\text{bulk}} \approx AC_\infty N^{\gamma-1}\mu_\infty^N \ . \tag{9}$$

Note that the bulk attrition parameter μ_∞ is not universal. As with Y_∞, we could "normalize" to have $C_\infty = 1$.

In the limit $\langle R_N^2\rangle \gg L^2$, the d^*-dimensional behavior with the appropriate exponent γ^* and modified attrition parameter μ_L, is expected. This leads to

$$C(y) \approx C_0 y^{\gamma-\gamma^*}\exp(-F_0 y^{-1}), \ \text{as } y \to 0 \ , \tag{10}$$

where C_0 and F_0 are universal, and

$$(c_N)_{\text{long chains}} \approx Aa^{\gamma-\gamma^*}C_0 L^{-\nu^{-1}(\gamma^*-\gamma)}N^{\gamma^*-1}\mu_L^N \ , \tag{11}$$

$$\mu_L \approx \mu_\infty(1 - F_0 a^{-1}L^{-1/\nu}) \ . \tag{12}$$

The increase in the free energy of a confined ($L < \infty$) chain, as compared with the bulk ($L = \infty$) system (due to reduced entropy), scales according to[1,13]

$$\frac{\Delta\mathcal{F}_N}{k_B T} \approx F(aN^{-1}L^{1/\nu}) \ , \tag{13}$$

where, by (7) and (8),

$$F(y) = -\ln[C(y)/C_\infty] \ . \tag{14}$$

Relation (13) is valid for "continuum" chains, as well as for the lattice systems. Scaling considerations cannot predict the rate of vanishing of $F(y)$ in the limit $y \to \infty$. A plausible guess would be a power law, $F(y) \sim y^{-\phi}$; however, this contribution will mix with corrections to scaling which are also inverse powers of N, typically. In the limit of small y, namely, for $\langle R_N^2\rangle \gg L^2$, we have, by (10),

$$F(y) \approx F_0 y^{-1} + (\gamma^* - \gamma)\ln y + \ln(C_\infty/C_0), \ \text{as } y \to 0 \ , \tag{15}$$

$$\left(\frac{\Delta\mathcal{F}_N}{k_B T}\right)_{\text{long chains}} \approx a^{-1}F_0 L^{-1/\nu}N - (\gamma^* - \gamma)\ln N + (\gamma^* - \gamma)\ln(aL^{1/\nu}) + \ln(C_\infty/C_0) \ . \tag{16}$$

The first term in (16) [and (15)] dominates[1,13] while all the other "scaling" terms may mix with correction-to-scaling contributions. However, the $(\gamma - \gamma^*)\ln N$ piece may be detectable, since corrections to scaling are normally *power-law* terms of the order lower than the leading $O(N)$ contribution in (16).

Relations (1) and (13) are equivalent[1] to

$$\langle R_N^2\rangle^{1/2} \approx Rf(R/L) \ , \tag{17}$$

$$\Delta\mathcal{F}_N/k_B T \approx g(R/L) \ , \tag{18}$$

where

$$R \equiv \langle R_N^2\rangle_{\text{bulk}}^{1/2} \ . \tag{19}$$

The hyperuniversality hypothesis in this formulation asserts that the dimensionless combinations $\langle R_N^2\rangle^{1/2}/R$, $\Delta\mathcal{F}_N/k_B T$, and R/L come with no nonuniversal factors *except those entering through* R [see (3)], so that f and g are both *universal* functions. Although intuitively appealing, this conclusion goes beyond the ordinary scaling; it is related[9] to the validity of hyperscaling relations and, in general, breaks down above the upper critical dimension. Beyond the question of metric factors, the mere use of single-scaling-combination forms like (17) and (18) may be an oversimplification[17] above d_c. Finally, let us mention that the study of ideally diluted polymer solutions (namely, noninteracting or isolated chain problem) is just the first step toward understanding the relevant experiments[1,18] which also probe interactions between the chains[1,7] and some dynamical properties.[19]

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